Cyclopenta[1,2-b:5,4-b′]dithiophene-Porphyrin Conjugates for Dye-Sensitized Solar Cells: A D-π-D-A Approach

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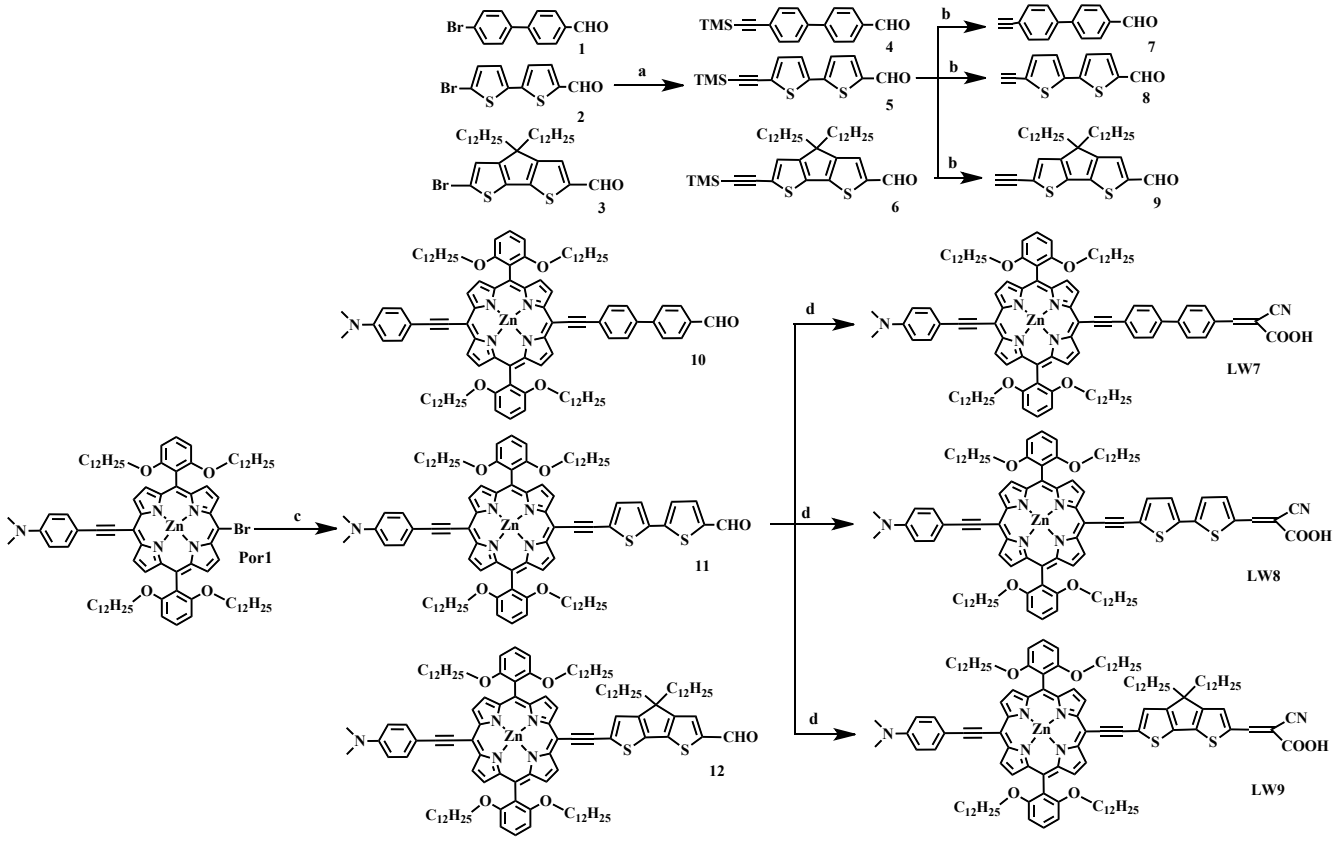
1.1 Chemicals:

All solvents and reagents, unless otherwise stated, were of analytical grade quality and used as received. Standard Schlenk techniques were employed to manipulate oxygen- and moisture-sensitive chemicals. The starting reagents ethyl 4'-bromo-[1,1'-biphenyl]-4-carbaldehyde (compound **1**), 5'-bromo-[2,2'-bithiophene]-5-carbaldehyde (compound **2**), 6-bromo-4,4-didodecyl-4H-cyclopenta [1,2-b:5,4-b']dithiophene-2-carbaldehyde (compound **3**) and 5-bromo-15-(4-N,N-dimethylamino- phenyl) ethynyl-10,20-bis[2,6-di(dodecyloxy)phenyl]porphyrin zinc(II) (coded as **Por-1**) was synthesized according to the literature.[1-5] Tetrahydrofuran (THF) was dried with sodium sand, and benzophenone indicator, dichloromethane (DCM), ether, triethylamine (TEA) were dried out with calcium hydride before using. Reactions were carried out under a dry nitrogen atmosphere. ^{1}H NMR and ^{13}CNMR spectra were measured on a Bruker-AF301 AT 400MHz spectrometer. High resolution mass spectra (HRMS) were measured with a Bruker micro TOF mass spectrometer.

1.2 Synthesis of LW7-9

The preparation of Zinc porphyrins sensitizers LW7-9 was achieved by a convergent synthesis (Scheme S1), which has been designed according to the Sonogashira coupling reactions.[6]



Scheme S1. Synthesis of LW7-9 a) TMSA, $Pd(PPh_3)_4$/CuI, TEA/THF, 18 h, 45 °C; b) K_2CO_3, MeOH, room temperature, 6 h; c) $Pd(PPh_3)_4$/CuI, THF/TEA, 50 °C, 12 h; d) cyanoacetic acid, piperidine, $CHCl_3$, reflux, 12 h.

Synthesis of 4'-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-4-carbaldehyde (4). Compound **4** was prepared under modified conditions of literature procedure.[1] To an ice-cooled mixture solution of 4'-bromo-[1,1'-biphenyl]-4-carbaldehyde (compound **1**, 261 mg, 1.0 mmol) in freshly distilled triethylamine (10 mL) and CH_2Cl_2(10 mL) was added CuI (10 mg, 0.04 mmol), $Pd(OAc)_2$ (10 mg, 0.04 mmol) and PPh_3 (32 mg, 0.11 mmol). After the solution was stirred for 30 min at 0 °C, trimethylsilylacetylene (0.32 mL, 2.25 mmol) was then added and the suspension was stirred for 30 min in an ice bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was heated to 45 ^oC for 24 h. The solution was then allowed to cool to room temperature and the solvent mixture was evaporated in vacuum. The crude product was purified by column chromatography on silica gel with a solvent combination of CH_2Cl_2/hexane (1:1, v/v) as eluent to provide **4** as a yellow solid (195 mg, 70%).. ^1H NMR ($CDCl_3$) δ 10.08 (s, 1H), 7.98 (d, J= 8.0 Hz, 2H), 7.60 (dd, J= 19.4 Hz, 4H), 0.30 (s, 9H). MS (APCI) m/z: calcd for 278.42; found 278.2.

5'-((trimethylsilyl)ethynyl)-[2,2'-bithiophene]-5-carbaldehyde (5). The synthetic procedure was similar to that of **4**. **5** was isolated as a yellow powder (73%). ^1H NMR ($CDCl_3$) δ 9.89 (s, 1H), 7.69 (d, J= 3.9 Hz, 1H), 7.21 (d, J= 4.0 Hz, 1H), 7.13 (d, J= 4.0 Hz, 1H), 7.06 (d, J= 4.0 Hz,1H), 0.27 (s, 9H). MS (APCI) m/z: calcd for 290.48; found 290.3.

Synthesis of 4,4-didodecyl-6-((trimethylsilyl)ethynyl)-4H-cyclopenta[1,2-b:5,4-b'] dithiophene-2-carbaldehyde (6).[2] The synthetic procedure was similar to that of **4**. **6** was isolated as a red solid (73%). ^1H NMR ($CDCl_3$) δ 9.87 (s, 1H), 7.58 (s, 1H), 7.17 (s, 1H), 1.87 (m, 4H), 1.54 (m, 4H), 1.36 (m, 24H), 1.28 (m, 12H), 0.90 (m, 6H), 0.30 (s, 9H). MS (APCI) m/z: calcd for 639.12; found 638.8.

Synthesis of 4'-ethynyl-[1,1'-biphenyl]-4-carbaldehyde (7). **Compound 7** was prepared under modified conditions of literature procedure.[4] Compound **4** (0.278 g, 1.0 mmol) and K_2CO_3 (0.69 g, 5.0 mmol) were dissolved in 8 ml of MeOH. The reaction was stirred at room temperature for 6 h, and the solvent was removed under vacuum. The solid was redissolved in CH_2Cl_2 and was washed with aqueous $NaHCO_3$ three times. The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The yellow residue was purified by column chromatography (CH_2Cl_2/hexane = 1/1) afforded product **7** (0.202 g, 98%). ^1H NMR ($CDCl_3$) δ 10.09 (s, 1H), 7.98 (d, J=7.9 Hz, 2H), 7.78 (d, J=8.2 Hz, 2H), 7.63 (dd, J=17.9 Hz, 4H). MS (APCI) m/z: calcd for 206.24; found 206.1.

Synthesis of 5'-ethynyl-[2,2'-bithiophene]-5-carbaldehyde (8). The synthetic procedure was similar to that of compound **7**. Compound **8** was isolated as a yellow powder (98%). ^1H NMR ($CDCl_3$) δ 9.89 (s, 1H), 7.70 (d, J= 3.9 Hz, 1H), 7.27 (d, J= 4.2 Hz, 1H), 7.24 (dd, J= 8.8 Hz, 2H), 3.50 (s, 1H). MS (APCI) m/z: calcd for 218.29; found 218.1.

Synthesis of 4,4-didodecyl-6-ethynyl-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2-carbaldehyde (9). The synthetic procedure was similar to that of compound **7**. Compound **9** was isolated as a red solid (98%). ^{1}H NMR ($CDCl_3$) δ 9.87 (s, 1H), 7.58 (s, 1H), 7.17 (s, 1H), 3.55 (s, 1H), 1.87 (m, 4H), 1.54 (m, 4H), 1.36 (m, 24H), 1.28 (m, 12H), 0.90 (m, 6H). MS (APCI) m/z: calcd for 566.94.12; found 566.8.

Synthesis of compound 10. Compound **10** was prepared under modified conditions of literature procedure.[5] $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) was added into a solution of **Por-1** (149 mg, 0.1 mmol) and compound **7** (61 mg, 0.3 mmol) in fresh distilled THF (70.0 mL) and anhydrous TEA (6 mL) under N_2. The reaction was stirred at 50 ^{o}C for 12 h. The progress of the reaction was monitored with TLC. The solvent was removed under vacuum. The residue was purified on silica chromatograph using THF/hexane=1/15 as eluent. The product was re-crystallized from CH_2Cl_2/MeOH to give green solid of **10** (115 mg, 71%). ^{1}H NMR ($CDCl_3$/pyridine-d5) δ 10.05 (s, 1H), 9.55 (dd, J = 7.6 Hz, 4H), 8.80 (dd, J = 18.9 Hz, 4H), 8.10 (d, J = 8.1 Hz, 2H), 8.03 (d, J = 8.21 Hz, 2H), 7.78 (m, 6H), 7.68 (t, J = 8.5Hz, 2H), 7.01 (d, J = 8.5Hz, 4H), 6.82 (d, J = 8.7Hz, 2H), 3.84 (t, J =6.9Hz, 8H), 3.46 (s, 6H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J=7.3Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H). MS (APCI) m/z: calcd for 1622.65; found 1622.1.

Synthesis of compound 11. The synthetic procedure was similar to that of compound **10**. The product was re-crystallized from CH_2Cl_2/MeOH to give green solid of **11** (75%). ^{1}H NMR ($CDCl_3$/pyridine-d5) δ 10.05 (s, 1H), 9.57 (d, J = 4.3 Hz, 2H), 9.45 (d, J = 4.3 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H), 8.76 (d, J = 4.5 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.68 (m, 4H), 7.49 (d, J = 2.91 Hz, 1H), 7.39 (d, J = 2.91 Hz, 1H), 7.01 (d, J = 8.5Hz, 4H), 6.82 (d, J = 8.7Hz, 2H), 3.84 (t, J =6.9Hz, 8H), 3.46 (s, 6H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J=7.3Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H). MS (APCI) m/z: calcd for 1622.65; found 1622.1.

Synthesis of compound 12. The synthetic procedure was similar to that of compound **10**, the product was re-crystallized from CH_2Cl_2/MeOH to give green solid of **12** (76%).^{1}H NMR ($CDCl_3$/pyridine-d5) δ 9.87 (s, 1H), 9.58 (d, J = 4.3 Hz, 2H), 9.47 (d, J = 4.3 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H), 8.76 (d, J = 4.5 Hz, 2H), 7.84 (d, J = 4.5 Hz, 2H), 7.71 (t, J = 8.5Hz, 2H), 7.67 (s, 1H), 7.45 (s, 1H), 7.01 (d, J = 8.5Hz, 4H), 6.82 (d, J = 8.7Hz, 2H), 3.84 (t, J =6.9Hz, 8H), 3.46 (s, 6H), 1.99 (t, J= 17.0 Hz, 4H), 1.23 (m, 8H), 1.20-1.12 (m, 36 H), 1.10-1.01 (m, 26 H), 0.98-0.85 (m, 16H), 0.79 (t, J=7.3Hz, 20 H), 0.75-0.71(br, 8H), 0.60-0.53 (br, 16H), 0.47-0.40(br, 8H). MS (APCI) m/z: calcd for 1968.25; found 1968.0.

Synthesis of compound LW7. **LW7** were prepared under modified conditions of literature procedure.[7] 2-cyanoacetic acid (2.6 mg, 0.03 mmol) and piperidine (0.014 mL) in 4 mL of dry THF were added into a solution of **10** (16.1 mg, 0.01 mmol) and heated to reflux under argon N_2 for 8 h. After cooling to room temperature, H_2O was added and the crude product was extracted with dichloromethane. The organic layer was washed with water 3 times, then dried over Na_2SO_4 and

concentrated under reduced pressure. The crude was purified by column chromatography (silica gel, methanol/dichloromethane, 1/9) twice, and recrystallized from CH_2Cl_2/MeOH to give green solid (8 mg, 50%). ^{1}H NMR ($CDCl_3$/pyridine-d5) δ 9.57 (dd, J = 7.3Hz, 4H), 8.81 (d, J = 4.4Hz, 2H), 8. 77 (d, J = 4.4Hz, 2H), 8. 32 (s, 1H), 8.13 (d, J = 8.1 Hz, 2H), 8.03 (d, J = 8.3 Hz, 2H), 7.80 (m, 6H), 7.68 (t, J = 16.7 Hz, 2H), 6.92 (d, J = 8.7Hz, 4H), 6.83 (d, J = 9.0 Hz, 2H), 3.84 (t, J =13.0 Hz, 8H), 3.06 (s, 6H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J=7.3Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H). ^{13}HNMR ($CDCl_3$/pyridine-d5) 160.0, 151.8, 151.2, 150.5, 150.3, 150.0, 132.6, 131.7, 131.4, 130.7, 130.4, 129.8, 129.5, 121.5, 115.0, 112.1, 111.7, 105.2, 102.0, 97.6, 96.8, 94.9, 91.8, 68.6, 45.2, 40.2, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 25.2, 22.6, 14.0. MS (ESI) m/z: calcd for 1677.64; found 1677.1. Element alanalysis (%) calcd for $C_{108}H_{134}N_6O_6Zn$, C, 77.32; H, 8.05; N, 5.01; found C 77.39, H 8.13, N 4.98.

Synthesis of LW8. The product was re-crystallized from CH_2Cl_2/MeOH to give green solid of **LW7** (52%). ^{1}H NMR ($CDCl_3$/pyridine-d5) δ 9.57 (d, J = 4.5Hz, 2H), 9.45 (d, J = 4.5Hz, 2H), 8.79 (dd, J= 18.7 Hz, 4H), 8.32 (s, 1H), 7.82 (d, J =7.7Hz, 2H), 7.68 (t, J = 8.8Hz, 2H), 7.46 (d, J = 3.8 Hz, 2H), 7.49 (d, J = 3.5 Hz, 1H), 7.39 (s, 2H), 7.01 (d, J = 8.5Hz, 4H), 6.82 (d, J = 8.7Hz, 2H), 3.84 (t, J= 6.9 Hz, 8H), 2.90 (s, 6H), 1.21-1.04(m, 26H), 0.98-0.88 (m, 22H), 0.81 (t, J=7.3Hz, 12H), 0.78-0.71 (br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40 (br, 8H). ^{13}C NMR ($CDCl_3$/pyridine-d5) 159.9, 151.5, 151.0, 150.6, 150.2, 150.0, 132.9, 132.6, 131.1, 130.5, 129.6, 121.4, 115.4, 112.1, 105.2, 102.1, 100.5, 97.2, 96.8, 91.8, 87.8, 68.6, 65.0, 40.3, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 25.2, 22.6, 14.0. HRMS (M^+) m/z: calcd for 1689.69; found 1689.4. Element alanalysis (%) calcd for $C_{104}H_{130}N_6O_6S_2Zn$, C, 73.93; H, 7.75; N, 4.97; found C 73.98, H 7.82, N 4.88.

Synthesis of LW9. The product was re-crystallized from CH_2Cl_2/MeOH to give brown-green solid of **LW9** (63%). ^{1}H NMR ($CDCl_3$/pyridine-d5) δ 9.58 (d, J = 4.3 Hz, 2H), 9.47 (d, J = 4.3 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H), 8.76 (d, J = 4.5 Hz, 2H), 8.32 (s, 1 H), 7.84 (d, J = 4.5 Hz, 2H), 7.67 (m, 3 H), 7.43 (s, 1H), 7.00 (d, J = 8.5Hz, 4H), 6.80 (d, J = 8.7Hz, 2H), 3.84 (t, J =6.9Hz, 8H), 3.46 (s, 6H), 1.99 (t, J= 17.0 Hz, 4H), 1.23 (m, 8H), 1.20-1.12 (m, 36 H), 1.10-1.01 (m, 26 H), 0.98-0.85 (m, 16H), 0.79 (t, J= 7.3Hz, 20 H), 0.75-0.71(br, 8H), 0.60-0.53 (br, 16H), 0.47-0.40(br, 8H). ^{13}C NMR ($CDCl_3$/pyridine-d5) 160.0, 151.5, 151.0, 150.6, 150.2, 150.0, 132.9, 132.6, 131.7, 131.1, 130.4, 129.6, 129.5, 121.6, 115.0, 112.1, 105.2, 102.1, 100.5, 68.6, 65.0, 40.3, 31.8, 30.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 25.2, 24.7, 22.6, 14.1. MS (APCI) m/z: calcd for 2038.34; found 2038.3. Element alanalysis (%) calcd for $C_{129}H_{178}N_6O_6S_2Zn$, C, 76.01; H, 8.80; N, 4.12; found C 76.07, H 8.89, N 4.11.

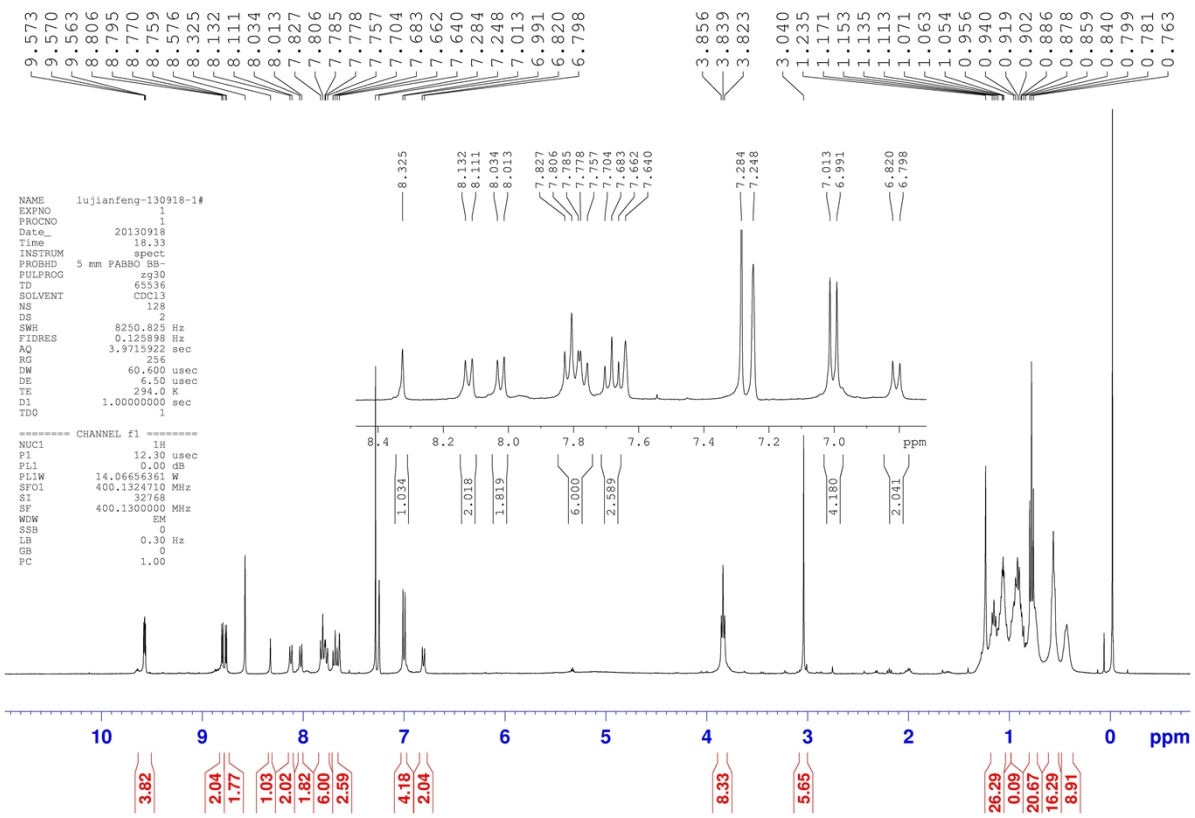


Fig. S1 ^{1}H NMR spectrum of LW7 (400 MHz, $CDCl_3$/pyridine-d5, 298 K).

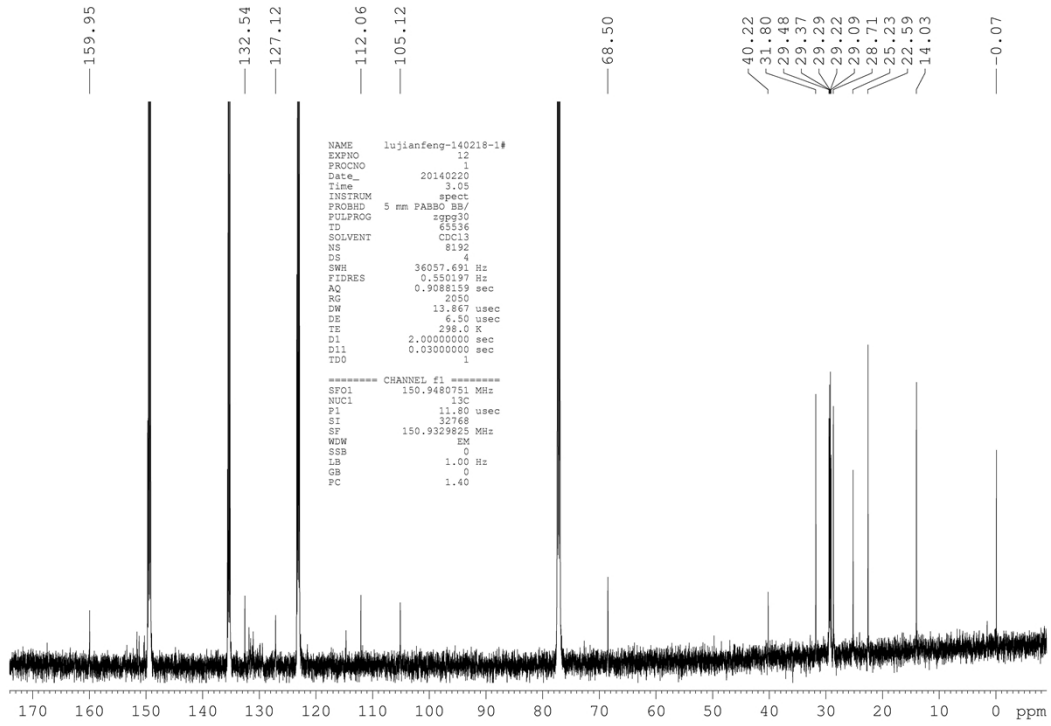


Fig. S2 ^{13}C NMR spectrum of LW7 (400 MHz, $CDCl_3$/pyridine-d5, 298 K).

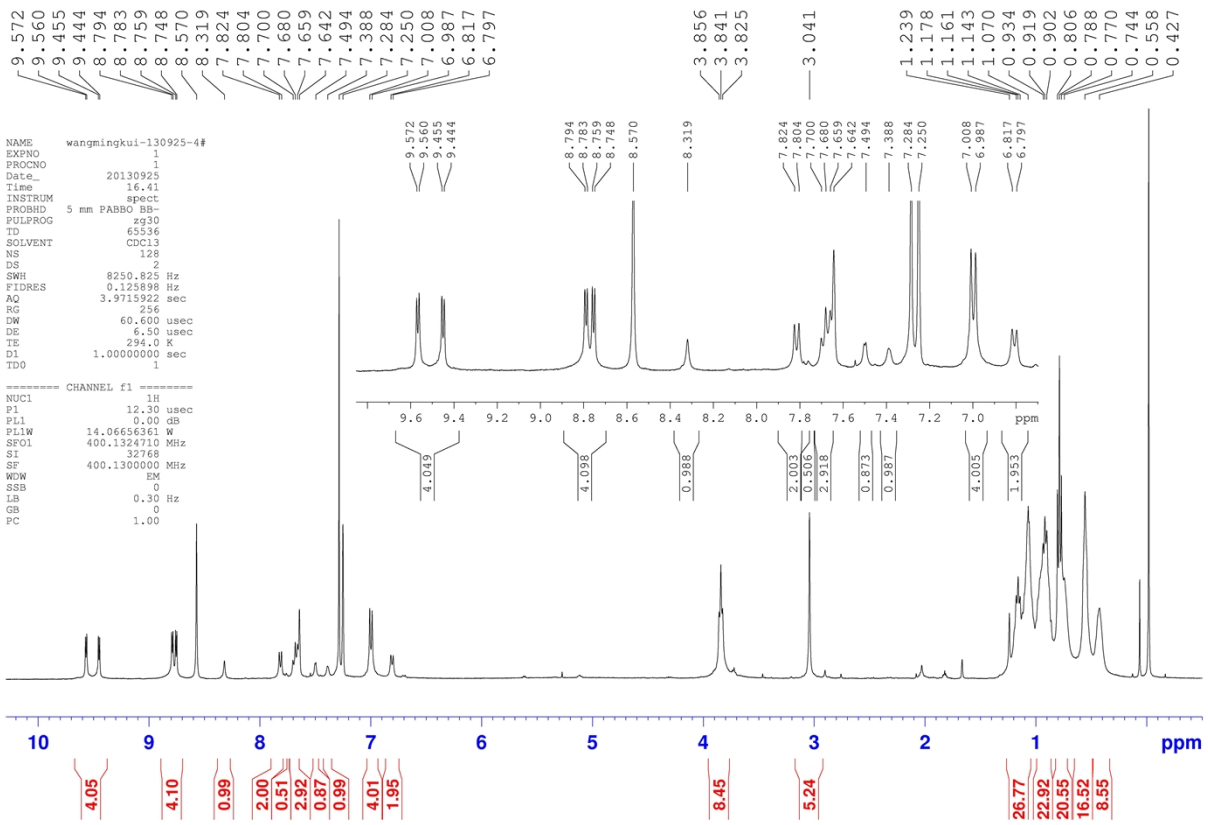


Fig. S3 ^{1}H NMR spectrum of LW8 (400 MHz, $CDCl_3$/pyridine-d5, 298 K).

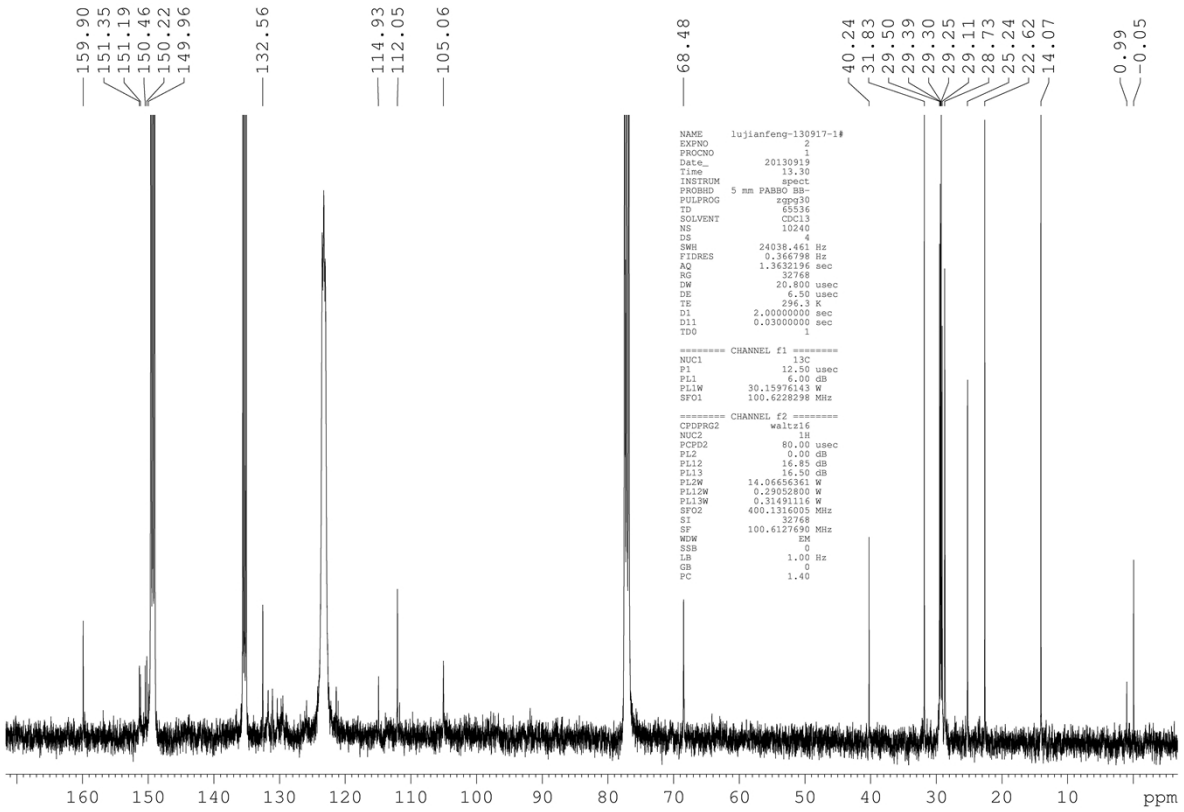


Figure S4. ^{13}C NMR spectrum of LW8 (400 MHz, $CDCl_3$/pyridine-d5, 298 K).

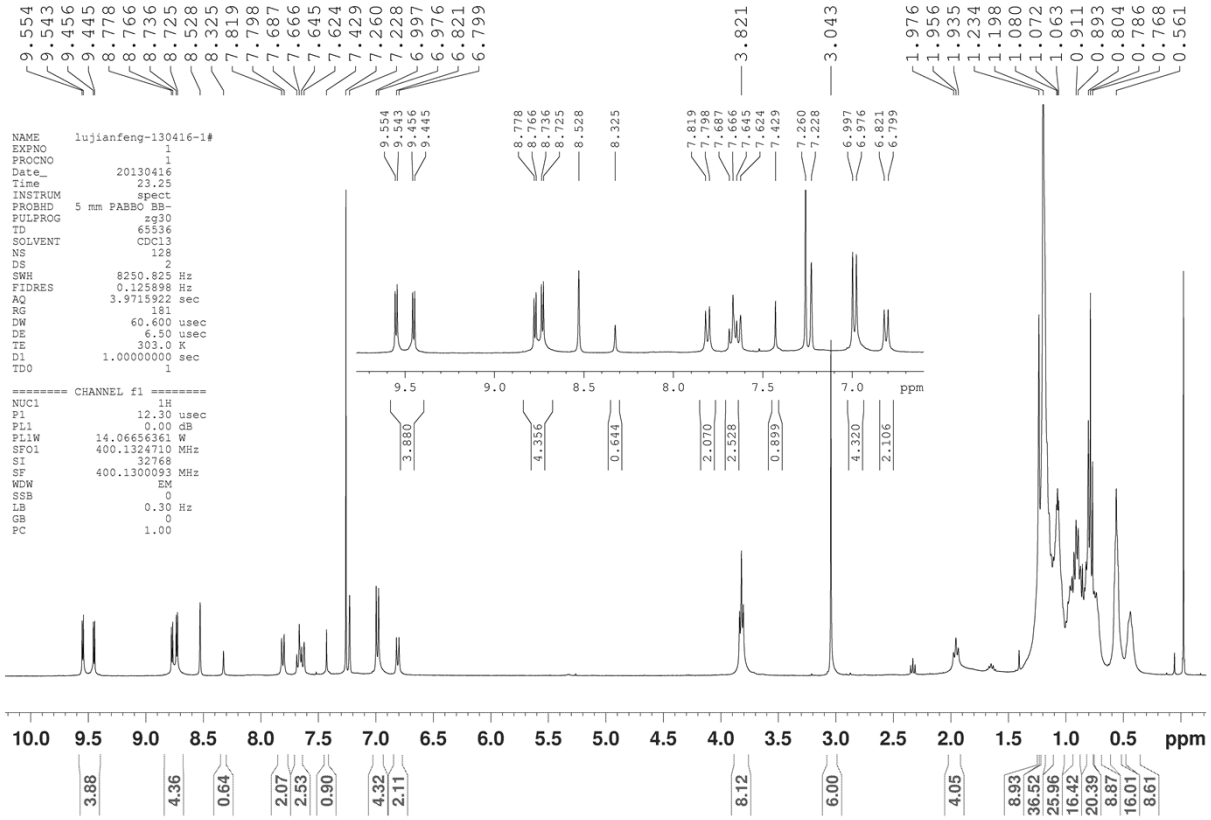


Fig. S5 ^{1}H NMR spectrum of LW9 (400 MHz, $CDCl_3$/pyridine-d5, 298 K).

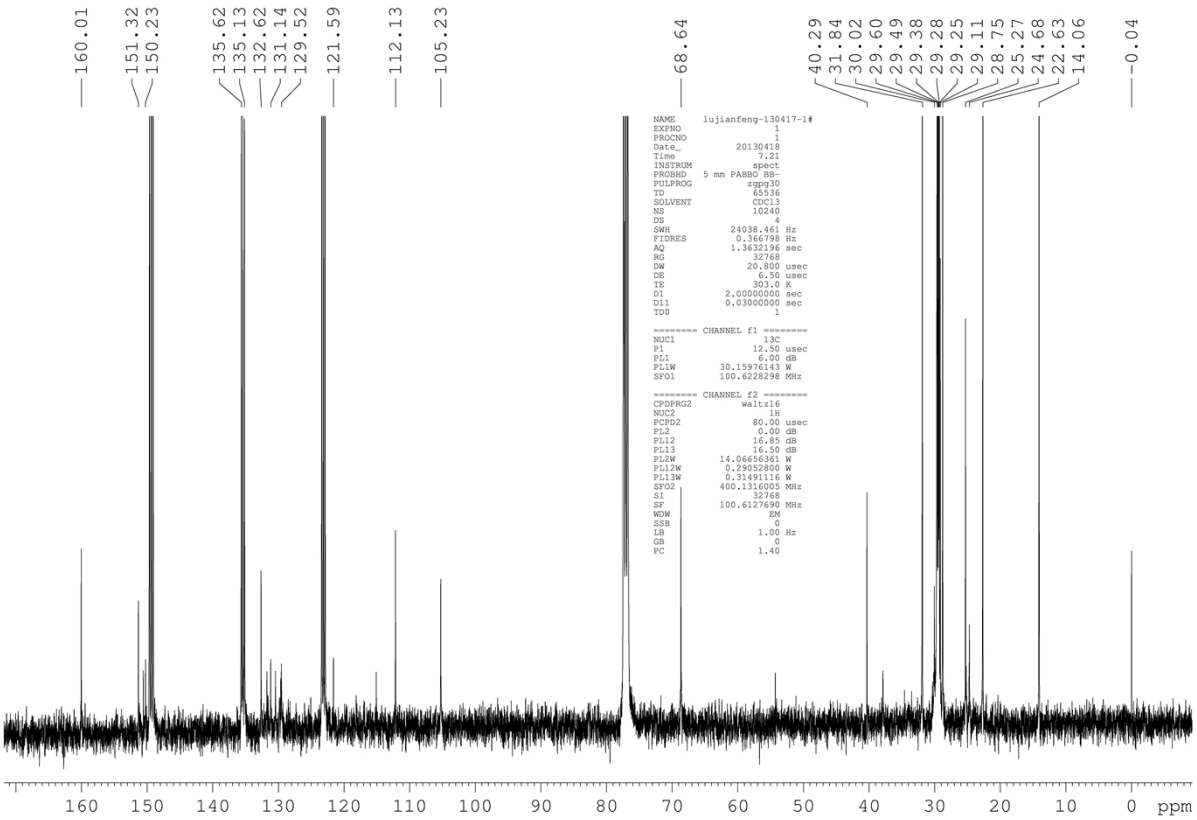


Fig. S6 ^{13}C NMR spectrum of LW9 (400 MHz, $CDCl_3$/pyridine-d5, 298 K).

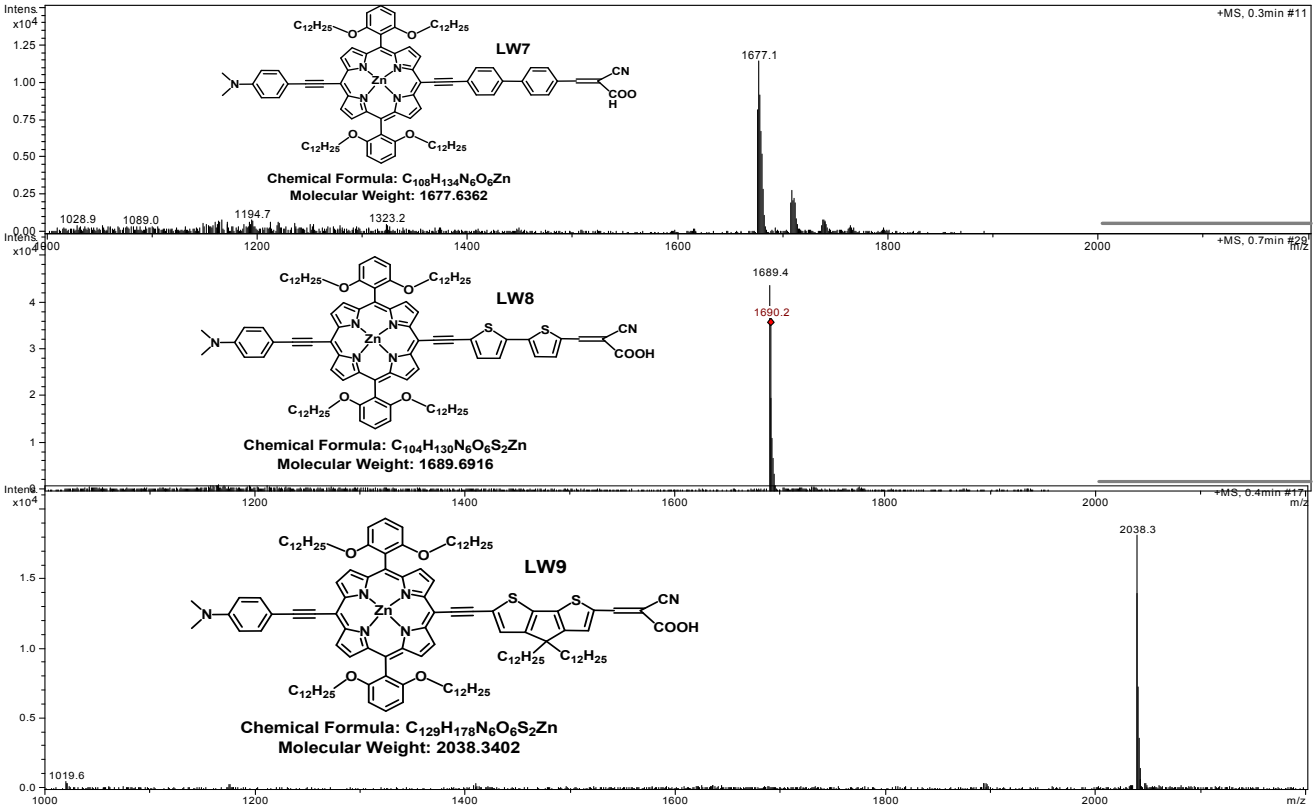


Fig. S7 Mass spectroscopy of LW7-LW9.

2. Spectroscopy measurements of LW7-9

The UV-visible absorption spectra were observed with a PE950 spectrophotometer and Fluorescent emission spectra were obtained with a Jasco FP-6500 spectrophotometer. Time-resolved luminescence of the porphyrins was recorded on Edinburgh instruments (FLSP920 spectrometers). The excitation light source centers at 445 nm, operated at a frequency of 10 MHz.

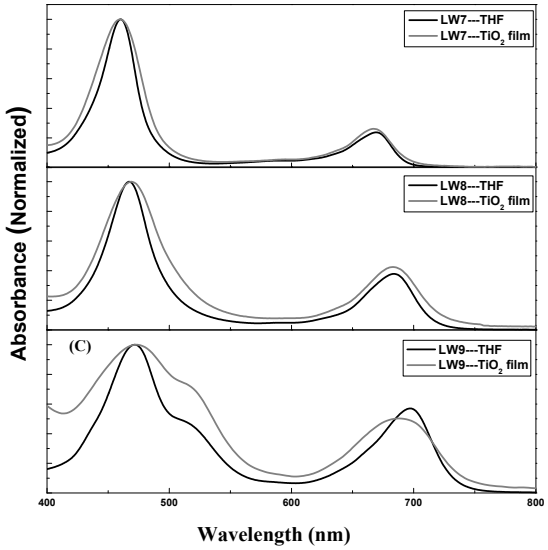


Fig. S8 Normalized UV-visible spectra of LW7-LW9 in THF (dark curve) and on TiO_2 films (transparent layers 2.3 μm thick of 20 nm TiO_2 particles) in air (grey curve).

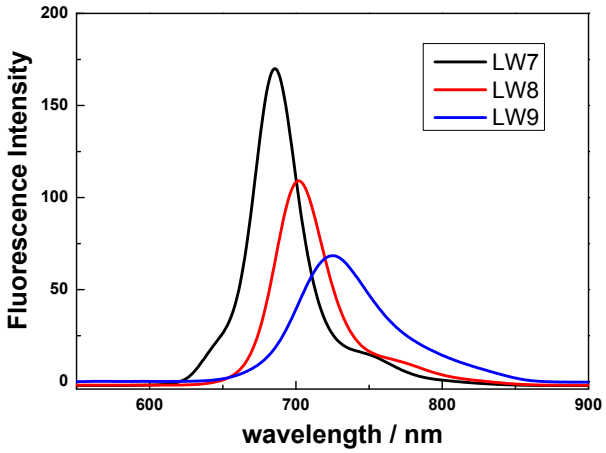


Fig. S9 Fluorescence emission spectra of LW7-LW9 in THF. The excitation wavelength: LW7, 461 nm; LW8, 467 nm; LW9, 471 nm

3. Electrochemical characterization of LW7-LW9

Square-wave voltammograms of various dyes were measured on a CHI660C electrochemical workstation. Glassy carbon electrode was used as the working electrode a platinum wire as the counter electrode, and Ag/AgCl (2 M LiCl in EtOH) as the reference electrode.

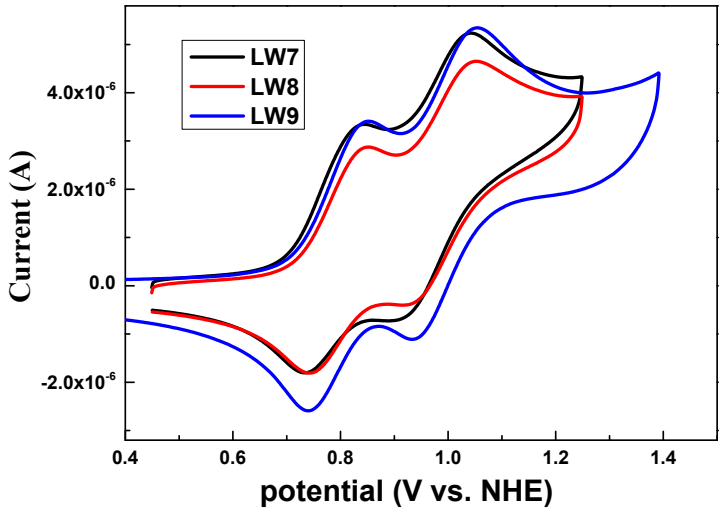


Fig. S10 Cyclic voltammograms of Zn(II)-porphyrin dyes in THF at a scan rate of 50 mV/s at room temperature with 0.1 M tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte.

4. The schematic energy-level diagram

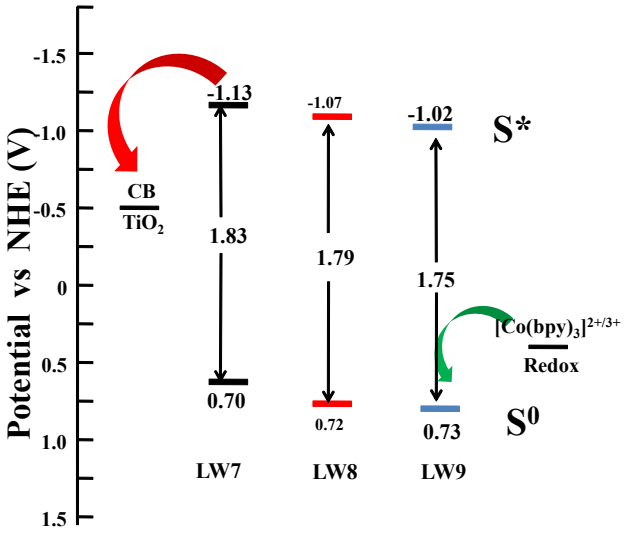


Fig. S11. Energy-level diagram of the LW7-LW9 porphyrins.

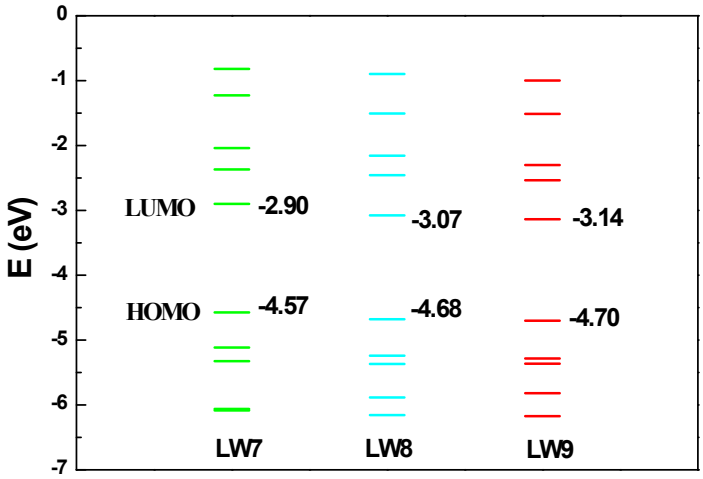


Fig. S12 Schematic energy-level diagram of the LW7-LW9 porphyrins by density-functional theory (DFT).

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